Magnetocaloric Effect in Ni–Cu–Mn–Gd–Ga Alloy. XI Symposium of Magnetic Measurements

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The magnetocaloric effect of the Ni–Cu–Mn–Gd–Ga polycrystalline alloy was investigated. The nominal composition of the alloy was $Ni_{50}Cu_{6.25}Mn_{16.75}Ga_{25}Gd_2$ at.%. The X-ray diffraction studies revealed presence of two phases at room temperature. This was confirmed by magnetic measurements conducted in low field of 4 kA/m (50 Oe), which showed two Curie transition temperatures, one in vicinity and the other one well above the room temperature. The analysis of isothermal magnetic curves allowed the calculation of magnetic entropy change (ΔS_M). Although the peak value of $|\Delta S_M|$ is relatively low, ≈1.1 J/(kg K), it is very broad. The adiabatic temperature change (ΔT) measured near room temperature is ≈0.49 K. Such result is irrespective of the magnetizing-demagnetizing cycle frequency which varied from 2/min to 10/min.

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1. Introduction

The magnetocaloric effect (MCE) occurs in all magnetic materials and refers both to the isothermal entropy change and to the adiabatic temperature change arising from the application or removal of a magnetic field H. The most appreciable effect occurs at temperatures near magnetic transitions, and depends strongly on the type of transition [1, 2]. In 1917, Weiss and Piccard were first who reported the reversible temperature change of 0.7 K when applying a field of 1200 kA/m (1.5 T) to the nickel sample near the Curie temperature (354 °C) [3]. The interest on the magnetocaloric properties of materials have renewed attention on the last decade since Brown [4] has shown that magnetic materials can be successfully applied to magnetic refrigeration at room temperature. In recent years, discovery of a giant magnetocaloric effect [5] has stimulated basic and applied interest in the development of new materials, including ferromagnetic Heusler alloys based on the X_2YZ formula. Those alloys undergo a structural (martensitic) transition and show also interesting magnetocaloric properties in the vicinity of the structural (T_M) and magnetic (T_C) transition points. The optimal magnetocaloric properties are shown when both, the martensitic and ferromagnetic transitions, are close to each other [6]. Both temperatures T_M and T_C, can be adjusted by tailoring the chemical composition. Replacing Mn with Cu in $Ni_2Mn_{1-x}Cu_xGa$, leads to coincidence of the two transition temperatures ($T_M = T_C = T_{MC}$), for $x = 0.25$ [7].

In this paper the MCE of the Gd-doped $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ polycrystalline alloy was investigated in order to check if such composite alloy (Gd-Heusler) is a good alternative to pure Gd or Heusler magnetocaloric materials.

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2. Experimental

Preparations of two alloys $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ and $Ni_{50}Mn_{16.75}Cu_{6.25}Ga_{25}Gd_2$ was conducted by induction melting of pure elements in argon atmosphere. After casting the ingots were homogenized at 1083 K for 48 h and slowly cooled with the furnace.

Chemical composition of the specimens was checked using the energy dispersive spectroscopy (EDS) technique.

Magnetic properties and transformation temperatures was measured using the LakeShore 7410 Vibrating Sample Magnetometer (VSM), equipped with a cryostat, at a magnetic field $H = 4$ kA/m (0.005 T) in the temperature range of 200–400 K. Heating and cooling rate of ≈2 K/min was applied.

The magnetic entropy changes (ΔS_M) were calculated, as in [8], using the experimental $M(T)$ curves and integrated Maxwell relation

$$\Delta S_M = \int(\partial M/\partial T)\,\mathrm{d}H. \quad (1)$$

The field induced temperature changes (ΔT) were recorded in direct measurement near room temperature (RT) at $H = 1600$ kA/m (2 T) using quasi-adiabatic regime.

3. Results

The transformation temperatures T_M and T_C, recorded at field $H = 4$ kA/m for both alloys are shown in Fig. 1. One can see that the Gd addition increased magnetization value. Such behaviour is related with strong ferromagnetic properties of Gd atoms which have a large localized magnetic moment [5]. Addition of Gd also slightly decreased the Curie point towards the room temperature, but dramatically decreased transformation temperature below RT.

The scanning electron microscopy (SEM) backscattered electrons (BSE) and energy dispersive spectroscopy (EDS) studies revealed the alloy containing Gd which exhibits two-phase structure at RT (Fig. 2). All

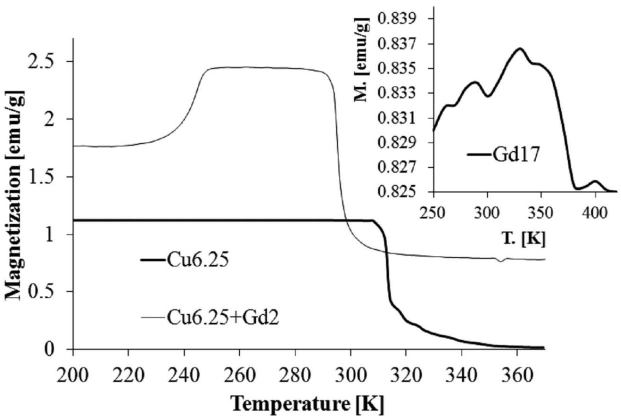

Fig. 1. Magnetization versus temperature for $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$, $Ni_{50}Mn_{16.75}Cu_{6.25}Ga_{25}Gd_2$ and $Ni_{46.8}Mn_{7.4}Cu_{11.1}Ga_{17.7}Gd_{17}$. (inset) alloys, $H = 4$ kA/m (0.005 Tesla).

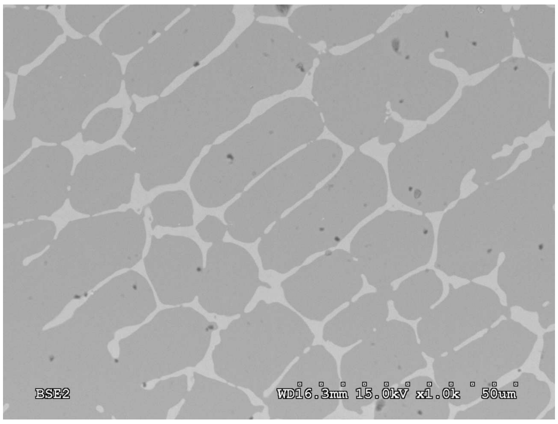

Fig. 2. BSE image of $Ni_{50}Mn_{16.75}Cu_{6.25}Ga_{25}Gd_2$alloy. Brighter area is Gd-rich phase $Ni_{46.8}Mn_{7.4}Cu_{11.1}Ga_{17.7}Gd_{17}$.

the Gd is located in the grain boundaries region forming Gd-rich phase — $Ni_{46.8}Mn_{7.4}Cu_{11.1}Ga_{17.7}Gd_{17}$.

The $|\Delta S_M|$ values calculated with formula (1) for $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ and $Ni_{50}Mn_{16.75}Cu_{6.25}Ga_{25}Gd_2$ are shown in Fig. 3. As we can see the value reaches up 12 J/(kg K) for $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ alloy, however the peak is very narrow. This phenomenon is a result of overlapping both transition temperatures and gives the Curie point the nature of first-order transition (rapid loss of magnetization) [7]. The Gd addition in $Ni_{50}Mn_{16.75}Cu_{6.25}Ga_{25}Gd_2$ alloy leads to separating both transition temperatures (Fig. 3b) which results in decreases of magnetic entropy changes. This separation can be observed as two peaks of the $|\Delta S_M|$ corresponding to both transitions (Fig. 1). The highest entropy change ≈1.5 J/(kg K), was recorded at structural transition temperature.

The ΔT measurement at $H = 1600$ kA/m (2 T) for both alloys, revealed significant temperature change at RT (Fig. 4). This phenomenon is corresponding with values of magnetic entropy change.

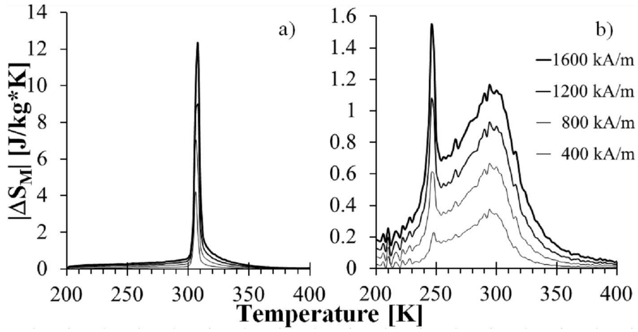

Fig. 3. Magnetic entropy changes calculated for (a) $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ and (b) $Ni_{50}Mn_{16.75}Cu_{6.25}Ga_{25}Gd_2$ alloys.

The $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ alloy shows large ΔS_M but peak is above the RT (308 K). Our measurement set is not capable of measuring the ΔT above RT but one could expect a peak value ≈1.5–2 K [7]. At RT $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ alloy shows very low value of $|\Delta S_M| \approx 0.7$ J/(kg K) which provide temperature change of ≈0.4 K (Fig. 4a).

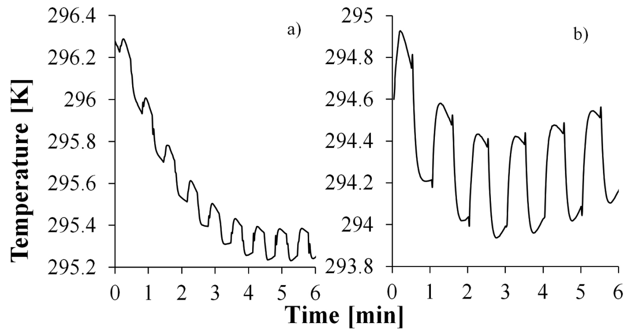

Fig. 4. The adiabatic temperature changes (ΔT) measured near RT at magnetic field of 1600 kA/m for (a) $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ and (b) $Ni_{50}Mn_{16.75}Cu_{6.25}Ga_{25}Gd_2$ alloys.

The Gd addition leads to decrease of $|\Delta S_M|$ peak value but shifts the Curie temperature towards the RT. It provides also higher $|\Delta S_M|$ at room temperature than $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ alloy. The ΔT value of ≈0.4 K was recorded for Gd-doped $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ alloy.

4. Conclusion

The Gd addition to $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ alloy separates martensite and Curie transformation temperatures. The Gd-doping also decreased slightly the Curie point towards the room temperature, but dramatically decreased structural transformation temperature below RT.

The peak values of $|\Delta S_M|$ and ΔT are ≈12 J/(kg K) and 0.2 K, ≈1.1 J/(kg K) and 0.49 K, for $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$and $Ni_{50}Mn_{16.75}Cu_{6.25}Ga_{25}Gd_2$ alloys, respectively.

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